

PREPARATION AND CHARACTERIZATION OF PALLADIUM CATALYSTS

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**Preparation and Characterization of Palladium Catalysts**

by

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**Preparation and Characterization of Palladium Catalysts**

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## Abstract

There is a critical need for improved combustion-oxidation catalysts to reduce emissions of toxic volatile organic compounds (VOCs) emitted from exhaust gas of gasoline combustion in automotive vehicles. Materials and systems currently available, such as the three way catalytic converter (TWC), have low activity below 400 °C in the catalytic process. Palladium catalysts were prepared by alternative methods including: preparation by wet impregnation or incipient wetness, drying by room temperature or air-oven, and support choice between silica and alumina. These catalysts were prepared to meet the demand for low temperature oxidation. Results indicated a 5% increase in percent dispersion of metal across the support due to room temperature drying conditions, a higher surface area and crystallite size favoring alumina or silica support, a much larger monolayer uptake for alumina supported catalysts, and characteristic site strength of 600 °C chemisorption characterized by temperature programmed desorption (TPD).

Platinum is considered to be the most active metal for hydrocarbon oxidation, other than palladium for the oxidation of lighter than pentane hydrocarbons. Most hydrocarbons produced from automotive combustion are light weight and under a five carbon skeleton. Palladium has been chosen over platinum due to the relatively larger percent dispersion over a desired support (1). However, it has not been resolved to use primarily one noble metal as the drive of this study, but rather as one piece of a survey of metals to undergo the achievement of an engineered catalyst effective for low temperature activity. This objective derives from an inherent problem of current automotive related catalysis which is the inefficiency of catalytic activity at ambient temperatures (2). Modern automotive vehicles utilize the three way catalytic converter (TWC) to



# Chapter 1

## Introduction

### *Automotive catalytic converters*

The primary catalysts used to currently reduce pollutants from vehicle and industrial exhaust are palladium, platinum, rhodium, and ruthenium. These metals dispersed onto the surface of alumina, thoria, or silica supports offer a variety of functions for combustion of volatile organic compounds (VOC). Palladium catalysts as well as other noble metal catalysts most often encounter VOCs such as carbon monoxide, nitric and nitrous oxides, ozone, hydrocarbons, and other non-halogenated VOCs in combustion environments. Combustion reactions release mostly harmless water vapor and carbon dioxide under high temperature conditions; however, the toxic VOC by-products released are a detriment to the environment and health. Therefore, it is necessary for these catalysts to be both robust and capable of efficient oxidation catalysis under high temperature conditions.

Platinum is considered to be the most active metal for hydrocarbon oxidation, other than palladium for the oxidation of lighter than pentane hydrocarbons. Most hydrocarbons produced from automotive combustion are light weight and under a five carbon skeleton. Palladium has been chosen over platinum due to the relatively larger percent dispersion over a desired support (1). However, it has not been resolved to use primarily one noble metal as the drive of this study, but rather as one piece of a survey of metals to undergo the achievement of an engineered catalyst effective for low temperature activity. This objective derives from an inherent problem of current automotive related catalysis which is the inefficiency of catalytic activity at ambient temperatures (2). Modern automotive vehicles utilize the three way catalytic converter (TWC) to



reduce the health risks and environmental impact of toxic by-products of the combustion of gasoline; it is composed of palladium, platinum, and rhodium metals dispersed on a cerium support. TWCs are highly effective at catalyzing oxidation reactions in the temperature range of 200-250°C but are catalytically inefficient at lower or ambient temperatures. Current emission standards in California require federal test procedure 75 (FTP-75) in which the emission of carbon monoxide must not emit more than 4.2 g/mi for every 100,000 miles driven; nitric oxides ( $\text{NO}_x$ ) must not exceed 0.6 g/mi for tier 1 loaded vehicle weight transportation (3). However, during cold starts the catalytic activity of the TWC drops low enough to emit nearly 90% of the toxic by-products. As a result, it has been of great interest for energy related engineering and environmental protection to prepare a catalyst effective at both the high operating range of current catalysts and at the lower temperature range encountered during a cold start.

There are several proposed solutions to the cold start problem (3). One solution offers an exponential increase in the heating time of the catalytic converter vessel by placing it closer to the combustion output. This results in a lower production of toxic material but greatly hinders the life of the catalyst which generally outruns the life of an automotive vehicle or engine. This is necessary due to the cost of precious metals. However, the prolonged exposure of the catalysts to a higher temperature range results in the decomposition of the catalyst and possible sintering, thus reducing activity. Another solution to the cold start is direct heating of the catalytic mantle. It is easily foreseen that this method requires a supply of additional energy and thus defeats the purpose of energy conservation; most of these catalysts have low thermal conductivities. A third method attempts to heat the catalyst bed as well by supplying a flammable mixture of hydrogen, air, and fuel in the exhaust stream after combustion. This stream of exhaust gas is then ignited and heats the catalyst chamber but results in the reduction of fuel economy of the system. A



fourth method has been proposed to prepare a catalyst capable of oxidizing toxic exhaust gas products to their harmless counterparts at ambient as well as high temperature ranges.

### *Theories of heterogeneous catalysis*

In catalysis, the rate of a chemical reaction is changed by a participating substance, the catalyst, by choosing a reaction path with lower activation energy and thus resulting in a higher reaction rate than would be observed in the uncatalyzed reaction at the same temperature. The result that the catalyst has on a reaction varies and depends on the surrounding species. A catalyst can speed a reaction millions of times faster but in the presence of an inhibitor the catalyst will slow the reaction, or in the case of a promoter, the catalytic activity can be increased further.

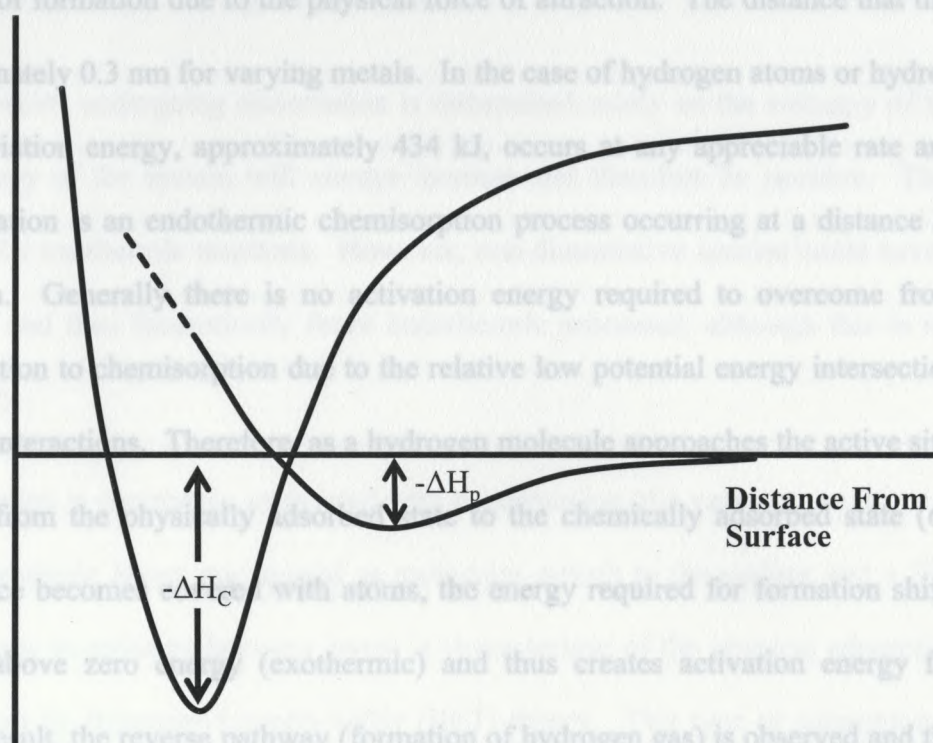
The catalysis involved in automotive combustion reactions encompasses the branch of heterogeneous catalysis in which the catalyst subsists in an alternate phase as the reactant medium. In the case of heterogeneous catalysis, it is important to clarify the nature of adsorption and the overall unifying theory of adsorption by the catalyst which is often overlooked and oversimplified.

### *Adsorption*

Adsorption can loosely be described as an uptake on the surface of a solid which is preceded by dissociation of a bond, such as the hydrogen – hydrogen bond in the case of hydrogen gas ( $H_2$ ). When the interaction is chemical it is a process called chemisorption and when the interaction is physical it is described as physisorption. In the simplest case of  $H_2$ , the process of adsorption can be described by a Lennard – Jones potential energy diagram (4).



Potential Energy



Distance From Surface

**Figure 1.** Lennard-Jones potential energy diagram illustrating adsorption enthalpies for physical and chemical processes.

The Lennard-Jones energy diagram indicates the potential energy of hydrogen as a function of the distance from the metal surface. As shown in the figure above, as the distance between the molecules or atoms to the surface of the catalyst increases to infinity, the potential energy of the adsorption approaches zero; this inherent observation is logical since there are no interactions between two species at a great distance of separation. Conversely, as the distance of the molecules to the surface approaches zero, the potential energy goes to infinity due to great electrostatic repulsion-interactions between the adjoining atoms' electron cloud. In the case of adsorption is not only limited to metals but any nonmetal solid as well. However, chemisorption the hydrogen molecule, as the distance between analyte and catalyst decreases from infinity, Van der Waals attraction occurs and physisorption takes place (5). The force of this interaction is characteristic of the radii of the atoms and can be expressed as a sum of the atomic radii with according to Gibbs free energy.



endothermic enthalpy of formation due to the physical force of attraction. The distance that this takes place is approximately 0.3 nm for varying metals. In the case of hydrogen atoms or hydron ions, the initial dissociation energy, approximately 434 kJ, occurs at any appreciable rate and enthalpy heat of formation is an endothermic chemisorption process occurring at a distance of approximately 1.5 nm. Generally there is no activation energy required to overcome from transition of physisorption to chemisorption due to the relative low potential energy intersection of the two adsorption interactions. Therefore, as a hydrogen molecule approaches the active site, it transfers smoothly from the physically adsorbed state to the chemically adsorbed state (6). However, as the surface becomes covered with atoms, the energy required for formation shifts the potential barrier above zero energy (exothermic) and thus creates activation energy for chemisorption. As a result, the reverse pathway (formation of hydrogen gas) is observed and the catalyst becomes saturated. This concept is relatively important for palladium/hydrogen interactions since the noble metal palladium has a tendency to adsorb hydrogen in the bulk of its metal. As long as the activation energy of the system is retained to a close-to-zero potential energy, a slower process of hydrogen diffusion to unoccupied sites is allowed within the bulk and offer interstitial hydrogen atom a stable position. In essence, palladium exhibits a natural phenomenon of retaining hydrogen atoms above normal capacity for transition metals (7).

#### *Physicochemical adsorption*

In theory, chemisorption can take place between any molecular species in which adsorption is not only limited to metals but any nonmetal solid as well. However, chemisorption will only truly take place when the free energy of the system ( $\Delta G$ ) favors the spontaneous equilibrium, indicated by a negative value (8). The free energy of a system can be defined according to Gibbs free energy.



metallic surface area is generally unit  $\Delta G = \Delta H - T\Delta S$  analytic process since the rate of the 1

reaction generally corresponds to the rate of reactant adsorbing to the surface followed by gas diffusion, i.e. the rate determining step. For reactions that depend on the accessibility to the system since the entropy of the system will always increase and therefore be positive. Thus the adsorption of a species undergoing dissociation is determined solely on the enthalpy of the metal and thus the reaction rate on the surface of the support, the most stable and highest surface adsorption will occur for exothermic reactions. However, non-dissociative species could have a negative entropy gain and thus theoretically favor endothermic processes; although this is not manufactured, they are generally very unstable under reaction conditions and thus supported seen experimentally (9).

catalysts are preferred (14). Common supports used in catalysis are alumina, silica, zeolites,

Physical adsorption is commonly associated with condensation of a vapor on a surface to form a liquid layer. Multiple layers are formed as molecules adsorb to the surface and a film develops. The difference in enthalpy between layers is characteristic of the physical adsorption isotherms and is defined by Brunauer-Emmett-Teller (BET) theory. This type of adsorption is studied in the proximity of the boiling point of the liquid and is usually studied with the adsorption of nitrogen gas to the surface of a solid submerged in liquid nitrogen at ambient temperatures (10), (11). This is a standard experiment of BET theory and will be discussed further.

Surface and supports alumina ( $\text{Al}_2\text{O}_3$ ) is due to both Lewis and Brønsted acidic character. When

alumina is in its pure form, oxygen acts as a Lewis acid in the presence of water, typically from the atmosphere, by accepting the lone pair. Once alumina interacts with water, the  $\text{AlOH}$  species metal and even provide further oxidation potential through the support itself. There are acts as a Brønsted acid in that it dissociates a proton. Hydroxyl groups are found on alumina as unsupported catalysts as well, such as in the oxidation process of ammonia by finely woven well and behave in a similar manner and when combined with alumina can have a greater acidic platinum-rhodium gauze (12), (13). These gauze materials have also been used to oxidize gas character due to the weakening of OH bonds by silica (IV) and aluminum(III) centers (18). mixtures for the catalytic removal of volatile organic compounds (VOCs). To stabilize the unsupported metal catalysts, promoters are usually used as an anchor such as rhodium in the oxidation of ammonia, which slows down the surface rearrangement of platinum. However, the



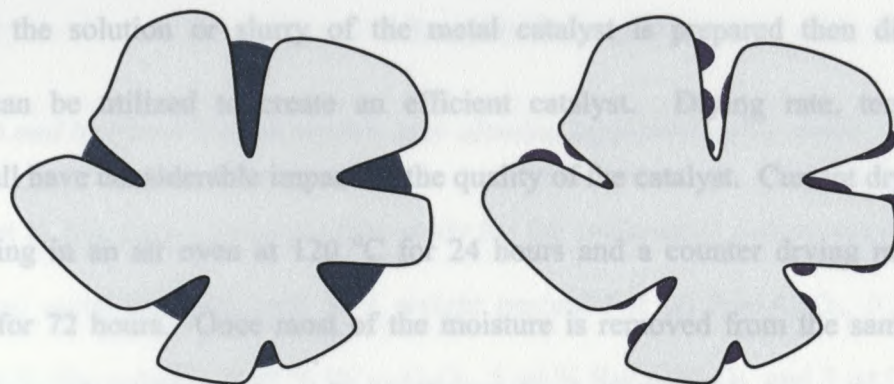
metallic surface area is generally unimportant in the catalytic process since the rate of the reaction generally corresponds to the rate of reactant adsorbing to the surface followed by gas diffusion, i.e. the rate determining step. For reactions that depend on the accessibility to the metal and thus the reaction rate on the surface of the support, the most stable and highest surface area catalysts are ideal. Although fine unsupported metal particles with high surface area can be manufactured, they are generally very unstable under reaction conditions and thus supported catalysts are preferred (14). Common supports used in catalysis are alumina, silica, zeolites, active carbons, and complex mixtures. These supports have pore diameters large enough to house the metal crystallites and allow free range of adsorption and releasing of catalyzed products. Furthermore, the support is not always inert and can promote activity, selectivity, and stability; however, the support does not catalyze any reaction unless the support is a catalytically active oxide, such as  $V_2O_5$  (15), (16). Some of the more inert catalysts, such as alumina and silica, have acidic properties and when used in conjugation can greatly influence selectivity of the catalyzed reaction. Silica-alumina supports, after undergoing specific calcination procedures, have strong acidic properties and are used in the isomerization catalysis of hydrocarbons (17). The acidic nature of alumina ( $Al_2O_3$ ) is due to both Lewis and Brönsted acidic character. When alumina is in its pure form, oxygen acts as a Lewis acid in the presence of water, typically from the atmosphere, by accepting the lone pair. Once alumina interacts with water, the  $AlOH$  species acts as a Brönsted acid in that it dissociates a proton. Hydroxyl groups are found on alumina as well and behave in a similar manner and when combined with alumina can have a greater acidic character due to the weakening of OH bonds by silica (IV) and aluminum(III) centers (18).



### *Preparation methods*

Upon preparation of supported catalysts, both the surface area and number of active sites available are crucial to the activity and efficiency of the catalyst. Nature has the tendency to form shapes with the least surface energy thus it is important to prepare the supported catalysts as to oppose the minimal surface area boundary found with mobile ion tenacity of the support at the Tamman temperature, which is roughly half of the melting temperature (19), (20). Impregnation is used to infuse the support material with the catalyst head; two primary techniques are used, wet impregnation and incipient wetness (dry impregnation). There is also the method of deposition-precipitation to introduce the catalyst before calcination but impregnation will be the primary concern for this research. Impregnated catalysts are prepared by introducing a solution into the pores of the support. Two interaction types transpire between the support and metal during impregnation: ion exchange may occur due to the acidic protons of the hydroxyl group on the surface of the support, or the exchange may be a more physical interaction with direct relation to the volume of pore size and aqueous solution make-up. Incipient wetness occurs if the volume of the metal solution is equal to or less than the pore volume of the support (21). The goal behind this method of impregnation is to retain the catalytic species to the pores during drying rather than upon initial interaction. The advantage of incipient wetness is control over the weight of added precursor to the catalyst. However, the homogeneity of the metal catalyst over the support may not be as uniform as wet impregnation as can be seen below.





**Figure 1.** Pore filling outcomes of wet and dry impregnation due to drying techniques.

If the volume of solution is greater than the pore volume of the support then the method is called wet impregnation. The drying process of the catalyst is vital due to the evaporation of water from the pores. If the catalyst is dried too quickly or harshly then the pore crevice may not uptake the entire metal bulk due to shifting of metal to the edges or outside of the pores (22).

These two methods are used to expedite capillary action of the metal into the pores of the support rather than the alternative and slower process, facilitated diffusion. Therefore, the two methods differ in the approach of adding the metal to the support material. Wet impregnation method involves the addition of metal solution to a slurry of support. Incipient wetness adds the same dilute metal solution to a dry support. The two methods offer means to promote capillary action based on the porosity of the support and the volume of the solution. The percent-by-weight of metal added to the support has a correlation to both percent dispersion and catalyst efficiency; however, a major stipulation in the percent weight is the price of the metals. Therefore, complete efficiency involves maximizing activity and minimizing cost. The percent weight of palladium chosen was 1% which falls into the general region of metal to support composition of industrial production (19).



Once the solution or slurry of the metal catalyst is prepared then different drying techniques can be utilized to create an efficient catalyst. Drying rate, temperature, and atmosphere all have considerable impact on the quality of the catalyst. Current drying procedure involves drying in an air oven at 120 °C for 24 hours and a counter drying method at room temperature for 72 hours. Once most of the moisture is removed from the sample, a thermal treatment process of calcination is applied to the catalysts. Calcination is a process that removes the volatile fraction within the support and metal solution by thermal decomposition. This is usually accomplished by applying appropriate temperature ramping and soaking conditions in an air environment and results in catalyst stability.

temperature programmed oxidation (TPO), temperature programmed reduction (TPR), O<sub>2</sub> chemisorption, and transmission electron microscopy (TEM). A comparative analysis of metal to support, weight-percent differences between 0.5 wt.% Ru/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 5 wt.% Ru/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> indicated similar particle size distribution based on TEM analysis but smaller amount of chemisorbed CO and O<sub>2</sub> per Ru metal for the higher weight catalyst showed much better CO oxidation. However, TPR and TPO results indicated that 0.5 wt.% Ru/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> can be oxidized at lower temperatures but can be reduced at higher temperatures compared to 5 wt.% Ru/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The BET surface area for the following metals were obtained 1 wt.% Pt/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 0.5 wt.% Ru/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 0.5 wt.% Rh/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 5 wt.% Pt/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 5 wt.% Ru/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and 5 wt.% Rh/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> yielding 94.0 (m<sup>2</sup>/g), 94.5, 105.4, 110.2, 87.1, and 115.0 m<sup>2</sup>/g respectively (23).

#### *Influence of catalyst treatments on the adsorption properties of alumina supported catalysts*

Diaz et al. has shown similar catalyst activity with alumina supported noble metals but characterized by the adsorption of *n*-alkanes, cycloalkanes, aromatics, and chlorinated compounds under different treatments such as reduction with hydrogen, oxidation with air and



## Literature Survey

*CO oxidation and hydrocarbon adsorption over alumina supported noble metals (Ru, Pt, Rh, Pd)*

Kim et al. has shown a comparative study for the preferential carbon monoxide oxidation over supported metal catalysts such as 1 weight percent (wt.%) Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 0.5 wt.% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 0.5 wt.% Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 5 wt.% Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 5 wt.% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and 5 wt.% Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Kim reported the highest preferential carbon monoxide oxidation as 5 wt.% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by reducing the high inlet CO at concentrations less than 10 ppm at low temperatures. The catalysts were characterized by carbon monoxide chemisorption in the absence and presence of H<sub>2</sub>, temperature programmed oxidation (TPO), temperature programmed reduction (TPR), O<sub>2</sub> chemisorption, and transmission electron microscopy (TEM). A comparative analysis of metal to support, weight-percent differences between 0.5 wt.% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 5 wt.% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> indicated similar particle size distribution based on TEM analysis but smaller amount of chemisorbed CO and O<sub>2</sub> per Ru metal for the higher weight catalyst showed much better CO oxidation. However, TPR and TPO results indicated that 0.5 wt.% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> can be oxidized at lower temperatures but can be reduced at higher temperatures compared to 5 wt.% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The BET surface area for the following metals were obtained 1 wt.% Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 0.5 wt.% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 0.5 wt.% Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 5 wt.% Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 5 wt.% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and 5 wt.% Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> yielding 94.0 (m<sup>2</sup>/g), 94.5, 105.4, 110.2, 87.1, and 115.0 m<sup>2</sup>/g respectively (23).

*Influence of catalyst treatments on the adsorption properties of alumina supported catalysts*

Diaz et al. has shown similar catalyst activity with alumina supported noble metals but characterized by the adsorption of *n*-alkanes, cycloalkanes, aromatics, and chlorinated compounds under different treatments such as reduction with hydrogen, oxidation with air and



treatment with inert gas. Diaz reported a change in the oxidation state of the active metal by differing treatment methods and the effect of adsorption of organic compounds in the presence of adsorbed hydrogen or oxygen. These effects were characterized by temperature programmed reduction, temperature programmed oxidation, and temperature programmed desorption. The oxidation of metal particles revealed Rh/Al<sub>2</sub>O<sub>3</sub> with a maximum peak at 420 °C, a low temperature peak occurred with Ru/Al<sub>2</sub>O<sub>3</sub> at 200 °C and no peak was observed for Pt/Al<sub>2</sub>O<sub>3</sub>. Furthermore, TPD of H<sub>2</sub> and O<sub>2</sub> saturated catalysts indicated that Rh/Al<sub>2</sub>O<sub>3</sub> does not adsorb hydrogen whereas Ru/Al<sub>2</sub>O<sub>3</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> exhibit continuous hydrogen desorption until 950 °C. The highest peaks were detected at 840 °C for Ru, 630 °C for Pt, and 470 °C for Ru alumina supported catalysts. The characterization of the adsorbed species was done by inverse gas chromatography (IGC) in the temperature range of 200 – 300 °C and the interaction parameters of polar molecules (benzene, chloroform, and trichloroethylene) were reported. The presence of chemisorbed hydrogen or oxygen on Pt hindered the adsorption of benzene more so than the adsorption of *n*-decane which showed competitive adsorption of O<sub>2</sub> and aromatic compounds. The heats of adsorption, entropies of adsorption, and free energy of adsorption were also reported (1).

#### *CO<sub>2</sub> reforming of CH<sub>4</sub>*

Portugal et al. investigated carbon dioxide reforming methane over Rh-containing catalysts. Rhodium was supported on γ-Al<sub>2</sub>O<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>, and TiO<sub>2</sub> and prepared by incipient wetness impregnation method. The catalysts were characterized by X-ray diffraction (XRD) spectroscopy, nuclear magnetic resonance (NMR), and temperature programmed desorption of hydrogen. The hydrogen to rhodium ratio for Rh catalysts decreased in the following order: Rh/Al<sub>2</sub>O<sub>3</sub> > Rh/Nb<sub>2</sub>O<sub>5</sub> > Rh/TiO<sub>2</sub> which was lower compared to those of the zeolite-supported



samples and therefore had lower dispersion of Rh particles on the amorphous supports. However, for oxide-supported catalysts there was no strong correlation between activity and metal dispersion of Rh particles on the various supports; it suggested that activity on oxide supports depended on the type of support and alumina showed the highest specific activity. It was found that the effect of the protons on the destabilization of the zeolite framework was higher in the case of higher silicon/aluminum ratios due to the dealumination of the zeolite. Thus, neutralization of the protons by a strong base lead to the stabilization of dispersion and zeolite structure. Also, oxide-supported Rh catalysts were more active compared to zeolite-supported ones due to a higher degree of participation of the reverse water – gas shift reaction (24).

#### *Pd/CeO<sub>2</sub> and TiO<sub>2</sub> catalyst for CO oxidation at low temperature*

Zhu et al. have prepared Pd/TiO<sub>2</sub>, Pd/CeO<sub>2</sub>, and Pd/CeO<sub>2</sub> – TiO<sub>2</sub> catalysts for the low temperature carbon monoxide oxidation by sol – gel precipitation followed by supercritical fluid drying. These catalysts were characterized by nitrogen adsorption, X-ray diffraction, diffuse reflectance infrared Fourier transform spectroscopy of carbon monoxide adsorption, and temperature programmed reduction with hydrogen and carbon monoxide. The preparation method produced finely dispersed PdO particles on the support surface with a high surface area outcome. Infrared spectroscopy showed CO adsorption that supported the hypothesis that Pd<sup>2+</sup> and Pd<sup>0</sup> species coexist in Pd/CeO<sub>2</sub>, but only Pd<sup>0</sup> was detected in Pd/TiO<sub>2</sub> and Pd/CeO<sub>2</sub> – TiO<sub>2</sub>. Temperature programmed reduction by hydrogen showed homogeneous CeO<sub>2</sub> mixture in CeO<sub>2</sub>/TiO<sub>2</sub> support. The reduction of CeO<sub>2</sub> – TiO<sub>2</sub> was determined to be more difficult than that of surface oxygen in the individual CeO<sub>2</sub> due to the formation of solid material. Carbon monoxide TPR resolved the limited reduction of PdO in PdO/TiO<sub>2</sub> on the support surface with



contrast to the complete reduction of PdO in Pd/CeO<sub>2</sub> – TiO<sub>2</sub> by carbon monoxide and was observed at ambient temperatures. Partial reduction of CeO<sub>2</sub> was associated with this reduction and indicated Pd – Ce – Ti interactions within the support and favorable reduction of PdO and interfacial CeO<sub>2</sub> species (25). The following techniques were used to address the goal and research questions:

1. Preparation of palladium catalysts by different methods.
2. Characterization of the catalysts.

#### Research Questions

- a. Do preparative methods alter total surface area of a catalyst?
- b. Do preparative methods change dispersion of the metal on the surface of a catalyst?
- c. Do preparative methods alter metal surface area of a catalyst?
- d. Do preparative methods have an effect on nature of active sites in a catalyst?
- e. Do preparative methods have an effect on strength of adsorption of a catalyst?

#### Methodology

Preparation of catalysts used in oxidation reactions of combustion exhaust depends on the metal precursor, the support chosen, method of infusing the metal to the surface of the support, the pH range of the solution, the drying technique, the calcination process, and reduction of impurities before characterization. The metal chosen for this study was palladium and supports were high porosity alumina and silica. There are two main methods to prepare these catalysts: wet impregnation and incipient wetness method. Tetraamminepalladium(II) nitrate solution (10 wt. % in H<sub>2</sub>O) was used as the metal precursor supplied by Sigma-Aldrich (CAS 13601-08-6).



## Chapter 2

### Goal

The preparation of a low temperature oxidation catalyst to oxidize carbon monoxide is the primary goal for this study. The following techniques were used to address the goal and research

questions:

1. Preparation of palladium catalysts by different methods.
2. Characterization of the catalysts.

### Research Questions

- a. Do preparative methods alter total surface area of a catalyst?
- b. Do preparative methods change dispersion of the metal on the surface of a catalyst?
- c. Do preparative methods alter metal surface area of a catalyst?
- d. Do preparative methods have an effect on nature of active sites in a catalyst?
- e. Do preparative methods have an effect on strength of adsorption of a catalyst?

### Methodology

Preparation of catalysts used in oxidation reactions of combustion exhaust depends on the metal precursor, the support chosen, method of infusing the metal to the surface of the support, the pH range of the solution, the drying technique, the calcination process, and reduction of impurities before characterization. The metal chosen for this study was palladium and supports were high porosity alumina and silica. There are two main methods to prepare these catalysts: wet impregnation and incipient wetness method. Tetraamminepalladium(II) nitrate solution (10 wt. % in H<sub>2</sub>O) was used as the metal precursor supplied by Sigma-Aldrich (CAS 13601-08-6).



Supports were fumed silica (CAS 112945-52-5) and  $\gamma$ -aluminum oxide (CAS 1344-28-1). A list of catalyst variables are shown in Table 1.

**Table 1.** Summary of prepared catalysts with respective methods.

Catalyst	Metal	Support	Loading	Method	Drying
A	Pd	Alumina	1.0%	Wet Impregnation	$\alpha$
B	Pd	Alumina	1.0%	Incipient Wetness	$\alpha$
C	Pd	Silica	1.0%	Incipient Wetness	$\alpha$
D	Pd	Silica	1.0%	Wet Impregnation	$\alpha$
E	Pd	Alumina	1.0%	Wet Impregnation	$\beta$
F	Pd	Alumina	1.0%	Incipient Wetness	$\beta$
G	Pd	Silica	1.0%	Incipient Wetness	$\beta$
H	Pd	Silica	1.0%	Wet Impregnation	$\beta$

#### *Incipient wetness method*

A solution of metal precursor (2.698 mL) was diluted in 30 mL of distilled water. Ten grams of support was placed in a beaker separately from the metal precursor. The metal was slowly added to the support with constant stirring. Once added, the catalyst slurry was allowed to stir for two hours at room temperature. Incipient wetness method of preparation resulted in a material that seemed to have a bulky composition. The paste appeared homogeneous after prolonged stirring.



### *Wet impregnation method*

A solution of metal precursor (2.698 mL) was diluted in 30 mL of distilled water. Ten grams of support was added slowly to the solution forming a thick paste. The catalyst slurry was stirred at room temperature for two hours. Observations indicated wet impregnation method of catalyst infusion resulted in a very smooth and uniform paste; a longer time was required to add the dry support than incipient wetness method.

### *Drying techniques*

Once the catalysts were prepared by their respective methods, two different drying techniques were employed and arbitrarily assigned designations  $\alpha$  or  $\beta$ . The drying method of these catalysts refers to temperature controlled pore exposure directly after method preparation by evaporating solvent particles at differing rates. The  $\alpha$ -drying method utilized an air oven to dry the catalysts to 120 °C for 24 hours. The  $\beta$ -drying method was a slower process that dried the catalysts at room temperature for a period of 72 hours. The catalysts were transferred to a desiccator until ready for calcination.

### *Calcination*

Temperature programming was used for calcination. The dried catalysts were placed in a mortar and pestle and crushed to centimeter sized particles and placed in ceramic boats. Catalysts were heated to 800 °C at 20 °C per minute and then soaked at 800 °C for four hours. The catalysts were brought to room temperature and placed in a desiccator for reduction and analysis; catalysts were crushed to powder before analysis.



### *Temperature programmed reduction*

Characterization and pretreatment of catalysts were performed on two separate equipment: Micromeritics Chemisorb 2705 (at Columbus State University) and Quantachrome Corporation ChemBET Pulsar (Quantachrome Instruments, Miami, FL). For analysis on Chemisorb 2705, argon was used as the carrier gas and hydrogen was used for treatment. Conversely, helium was used as the carrier gas and hydrogen was used for treatment with the Chemisorb 2705. The saturated catalyst was exposed to a gradient change in temperature at 10 °C/min to a limit of 750 °C. ChemBET Pulsar. Approximately one gram of catalyst sample was placed in a quartz capillary reactor in a continuous stream of argon. An oven was placed over the reactor and the temperature was raised to 120 °C at 20 °C/min and soaked at 120 °C for thirty minutes. The carrier gas was changed to pure hydrogen gas and the temperature was raised to 400 °C at 10 °C/min and soaked at 400 °C for two hours. The treatment gas was closed and pure argon was passed through the capillary at a maintained 400C for two hours, thus purging the reaction bed. The sample temperature was reduced to room temperature by fan after TPR and prepared for pulse titration.

### *Pulse chemisorption/titration*

All pulse chemisorption experiments were accomplished by ChemBET Pulsar. The

1) Performance  
carrier gas used was argon and the analysis (injection) gas used was carbon monoxide. The flow of carrier gas was constant throughout the experiment and set between 80 and 90 a.u. on the flow meter. The injection volume of carbon monoxide was 250 mL and the detector current was 150 mA. Experiments were performed at 40 °C and actual atmospheric pressure was recorded. The peak length of titration pulses was set to a minimum of 60 min and a maximum of 300 min with sample

e) Pore volume: 0.0001 to 0.15 cm<sup>3</sup>



a fourth order attenuation. The reproducibility standard deviation limit was  $\pm 1.33\%$  dispersion and a 95% reproducibility limit of 2.77 or  $\pm 3.69\%$  dispersion.

b) Sensitivity: 10 position (dynamic range: 512) plus user selectable detector current  
*Temperature programmed desorption*

2) Temperature Control

Treated catalyst samples were saturated with hydrogen gas at room temperature by pulse chemisorption. Temperature programmed desorption (TPD) experiments were carried out with Chemisorb 2705. The saturated catalyst was exposed to a gradient change in temperature at 10 °C/min to a limit of 750 °C.

*Brunauer-Emmett-Teller (BET) physisorption*

d) Furnace cooling: forced air using built in fan  
e) Sub-ambient: optional gas heat exchanger and dual thermocouple  
Pretreated catalysts (see TPR) held in a capillary reactor were placed in an insulated chamber housing liquid nitrogen. Pure nitrogen was used as the analysis gas and helium gas was used as the carrier. Pulse titration procedures were implemented identically to carbon monoxide pulse chemisorption procedures with the exception of adsorbing species (nitrogen gas).

*Instrument specifications*

b) Specific volume: 0.0001 cm<sup>3</sup>/g  
ChemBET Pulsar (Quantachrome Instruments)

c) Total surface area: 0.2 to 280 m<sup>2</sup>

1) Performance

a) Volume adsorbed: 0.001 to >100 cm<sup>3</sup>

b) Specific volume: 0.0001 cm<sup>3</sup>/g

c) Total surface area: 0.1 to 280 m<sup>2</sup>

d) Specific surface area: 0.01 m<sup>2</sup>/g to upper limit set only by weighing accuracy of smallest sample

e) Pore volume: 0.0001 to 0.15 cm<sup>3</sup>



- f) Accuracy, volume:  $\pm 1\%$
  - g) Reproducibility: 0.5%
  - h) Sensitivity: 10 position (dynamic range: 512) plus user selectable detector current
- 2) Temperature Control
- a) Preparation temperature: up to 450 °C using quartz heating mantle; up to 1100 °C using high-temperature furnace
  - b) TPR/TPD heating rates: 1-100 °C/min (up to 500 °C); 1-50 °C/min (up to 750 °C); 1-30 °C/min (up to 1000 °C); 1-20 °C/min (up to 1100 °C)
  - c) Furnace control: via PC software
  - d) Furnace cooling: forced air using built in fan
  - e) Sub-ambient: optional gas heat exchanger and dual thermocouple

#### Pulse Chemisorb 2705 by Micromeritics Corporation

- 1) Performance
- a) Volume adsorbed: 0.001 to  $>100 \text{ cm}^3$
  - b) Specific volume:  $0.0001 \text{ cm}^3/\text{g}$
  - c) Total surface area: 0.2 to  $280 \text{ m}^2$
  - d) Specific surface area:  $0.02 \text{ m}^2/\text{g}$  limited only by weighing accuracy of smallest sample
  - e) Pore volume: 0.0001 to  $0.15 \text{ cm}^3$
  - f) Accuracy, volume:  $\pm 1.5\%$  with 0.5% reproducibility
  - g) Reproducibility: 0.5%
  - h) Pore volume: Typically better than  $\pm 3\%$
- 2) Temperature Control (identical to ChemBET Pulsar)



- a) Preparation temperature: up to 450°C using quartz heating mantle; up to 1100°C using high-temperature furnace
- b) TPR/TPD heating rates: 1-100 °C/min (up to 500 °C); 1-50 °C/min (up to 750°C); 1-30 °C/min (up to 1000 °C); 1-20 °C/min (up to 1100 °C)
- c) Furnace control: via PC software
- d) Furnace cooling: forced air using built in fan
- e) Sub-ambient: optional gas heat exchanger and dual thermocouple

Table 2 consolidates organized catalysts A through H for TPD characterization and percent dispersion. These catalysts were differentiated based upon the support used, the method of preparation, and the method of drying. Based upon carbon monoxide pulse chemisorption, alumina supported catalysts showed similar but slightly greater percent dispersions than its counter support silica, but not enough to exceed the standard deviation. However, there is a clear disparity between the drying methods and the percent dispersion of palladium over the surface of the support. There is clear evidence that the room temperature drying method has approximately a 5% larger dispersion. This could be due to amorphous surface formation with prolonged drying. However, further surface studies such as transmission electron microscopy (TEM) must be completed to understand the mechanism of this increase in metal dispersion and additional chemi/physicosorption techniques for additional activity studies to determine the crystallite character. Two catalysts were used to compare surface studies based on the support difference. Alumina appears to have improved pore frameworks over silica. The surface area and crystallite size of alumina supported catalysts are both larger than silica by approximately 10 m<sup>2</sup>/g and 20 Å respectively. The monolayer uptake describes the number of active sites that will promote the chemisorption reactions and appears to favor alumina over silica. Alumina has a monolayer



## Chapter 3

### Results and Discussion

Catalyst characterization data have been obtained by Brunauer-Emmett-Teller (BET) method of physisorption and carbon monoxide pulse adsorption. The monolayer uptake, pore size, surface area, and percent dispersion of both alumina and silica supported palladium catalysts are outlined in Table 2.

Catalyst	Metal	Support	Loading	Preparation Method	Drying Method	Percent Dispersion
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*Effect of preparation methods on total surface area by BET method and percent dispersion*

Table 2 consolidates organized catalysts A through H for TPD characterization and percent dispersion. These catalysts were differentiated based upon the support used, the method of preparation, and the method of drying. Based upon carbon monoxide pulse chemisorption, alumina supported catalysts showed similar but slightly greater percent dispersions than its counter support silica, but not enough to exceed the standard deviation. However, there is a clear disparity between the drying methods and the percent dispersion of palladium over the surface of the support. There is clear evidence that the room temperature drying method has approximately a 5% larger dispersion. This could be due to amorphous surface formation with prolonged drying. However, further surface studies such as transmission electron microscopy (TEM) must be completed to understand the mechanism of this increase in metal dispersion and additional chemi/physicosorption techniques for additional activity studies to determine the crystallite character. Two catalysts were used to compare surface studies based on the support difference. Alumina appears to have improved pore frameworks over silica. The surface area and crystallite size of alumina supported catalysts are both larger than silica by approximately 10 m<sup>2</sup>/g and 20 Å respectively. The monolayer uptake describes the number of active sites that will promote the chemisorption reactions and appears to favor alumina over silica. Alumina has a monolayer



uptake of 9.13  $\mu\text{mole/g}$  which can accommodate approximately 20% more molecules than its counterpart silica. The physisorption capacity for these catalysts is shown by the BET analysis. Both alumina and silica supports show similar capabilities as efficient catalytic supports with values of 93.8  $\text{m}^2/\text{g}$  and 91.3  $\text{m}^2/\text{g}$  respectively.

**Table 2.** Characterization data of catalysts prepared by different methods and supports. Drying methods varied by oven in air at 120 °C ( $\alpha$ ) and room temperature drying ( $\beta$ ) prior to calcination process.

Catalyst	Metal	Support	Loading	Preparation Method	Drying Method	Percent Dispersion
A	Pd	Alumina	1.0%	Wet Impregnation	$\alpha$	10 $\pm$ 1.3%
B	Pd	Alumina	1.0%	Incipient Wetness	$\alpha$	10 $\pm$ 1.3%
C	Pd	Silica	1.0%	Incipient Wetness	$\alpha$	9 $\pm$ 1.3%
D	Pd	Silica	1.0%	Wet Impregnation	$\alpha$	9 $\pm$ 1.3%
E	Pd	Alumina	1.0%	Wet Impregnation	$\beta$	16 $\pm$ 1.3%
F	Pd	Alumina	1.0%	Incipient Wetness	$\beta$	15 $\pm$ 1.3%
G	Pd	Silica	1.0%	Incipient Wetness	$\beta$	15 $\pm$ 1.3%
H	Pd	Silica	1.0%	Wet Impregnation	$\beta$	14 $\pm$ 1.3%
	Metal	Support	Monolayer Uptake	Surface Area	Crystallite size	BET
B	Pd	Alumina	9.13 $\mu\text{mole/g}$	43.30 $\text{m}^2/\text{g}$	115.28 Å	93.8 $\text{m}^2/\text{g}$
C	Pd	Silica	7.34 $\mu\text{mole/g}$	34.78 $\text{m}^2/\text{g}$	95.70 Å	91.3 $\text{m}^2/\text{g}$

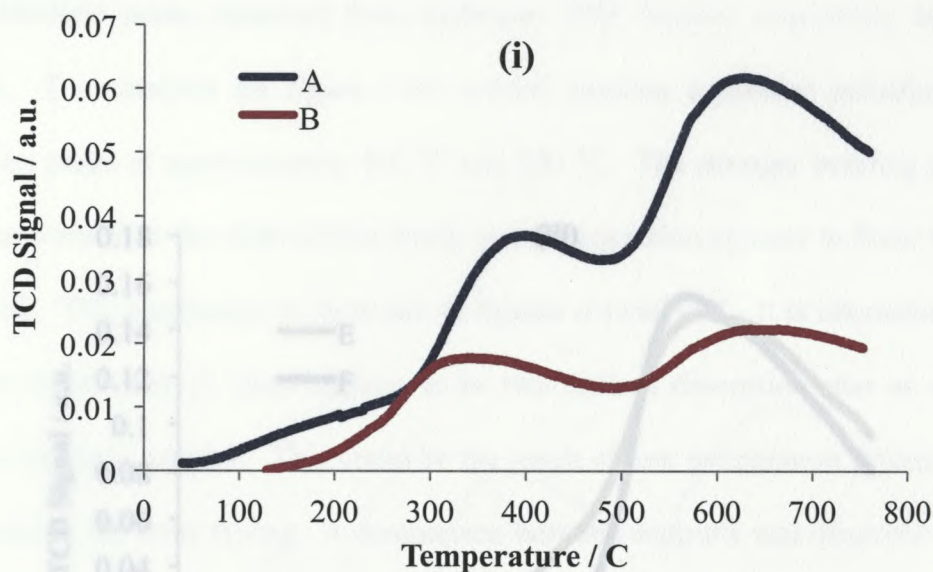
#### *Site strength by temperature programmed reduction and temperature programmed desorption*

Site strength characterization has been completed by temperature programmed desorption (TPD) technique of chemisorption. This method of characterization allows the determination of the Sabatier individuality of a catalyst by metal-analyte bonding strength at various surface sites

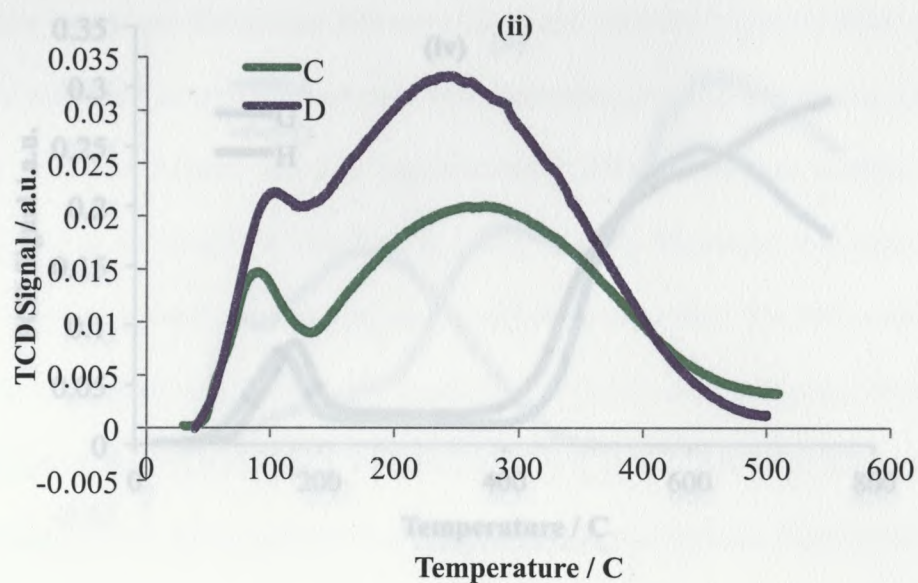


over the support. Bonding strength between metal and analyte is necessary for all adequate catalysis reactions but depends greatly on the surrounding conditions. The overall strength of each preparation parameter can be compared with TPD measurements and therefore the support, method of preparation, and drying method were each compared. Figures *i-iv* compared wet impregnation and incipient wetness methods of metal permeation.

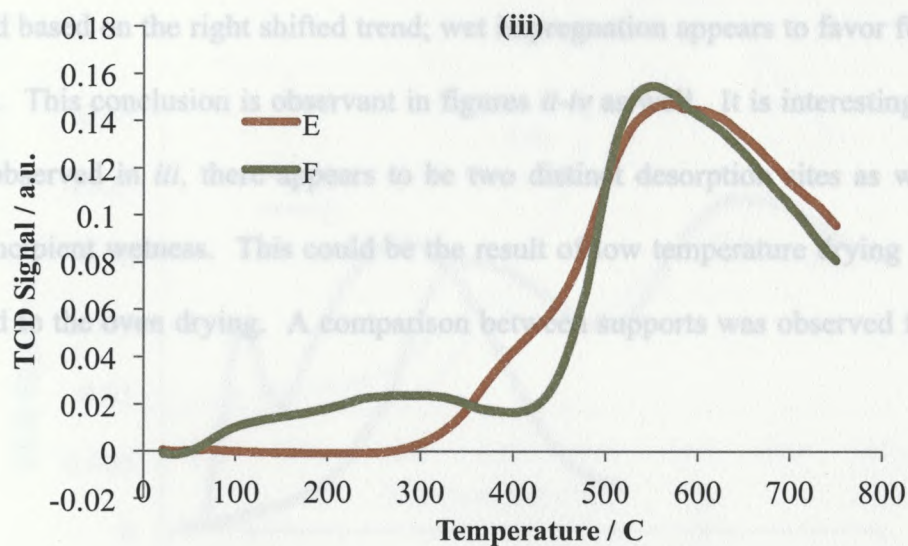
**Figures (i-viii).** Plots of thermal conductivity detector (TCD) signal vs. temperature [difference between preparation methods (*i, ii, iii, iv*); alumina vs. silica support (*v, vi*); drying methods (*vii, viii*)].



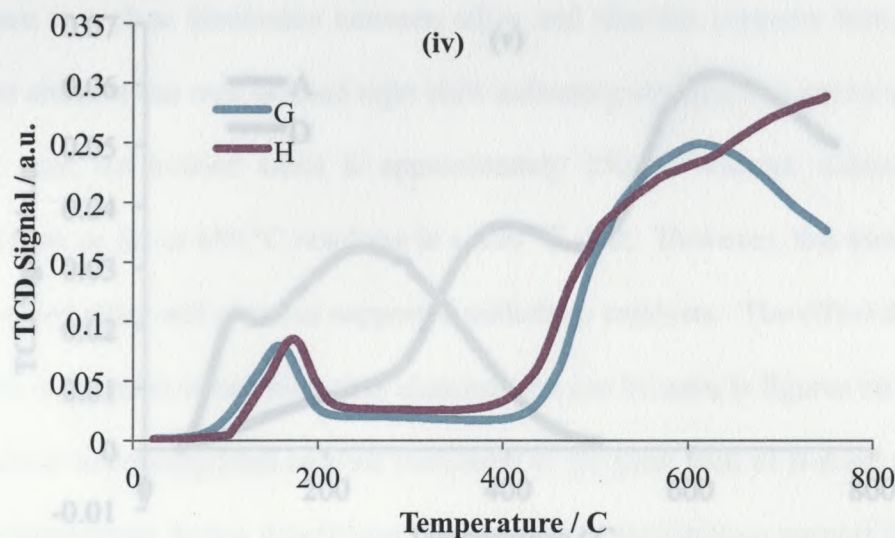




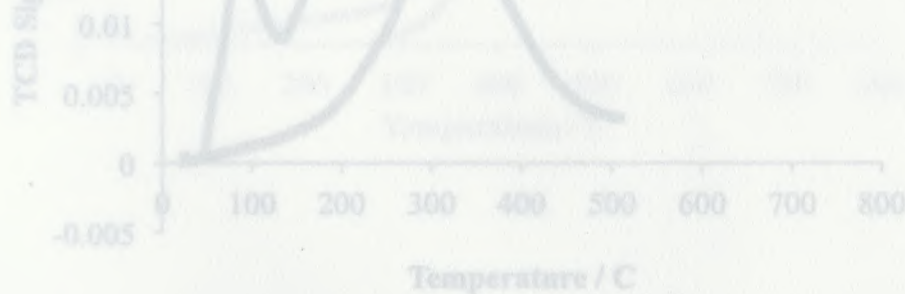
Multiple peaks observed from hydrogen TPD disclose availability based on bonding strength. The catalysts for figure 1 are  $\alpha$ -dried alumina supported palladium catalysts with desorption peaks at approximately 400 °C and 650 °C. The stronger bonding site is revealed at 650 °C and has the right shifted trend; wet regeneration appears to favor full metal surface protrusion. This conclusion is observant in figures ii-iv as well. It is interesting to note that for catalysts of figure iii, there appears to be two distinct desorption sites as well as a sharper peak for incipient wetness. This could be the result of low temperature drying of the  $\beta$ -method as opposed to  $\alpha$ -drying. A comparison between supports was observed for figures v and vi.



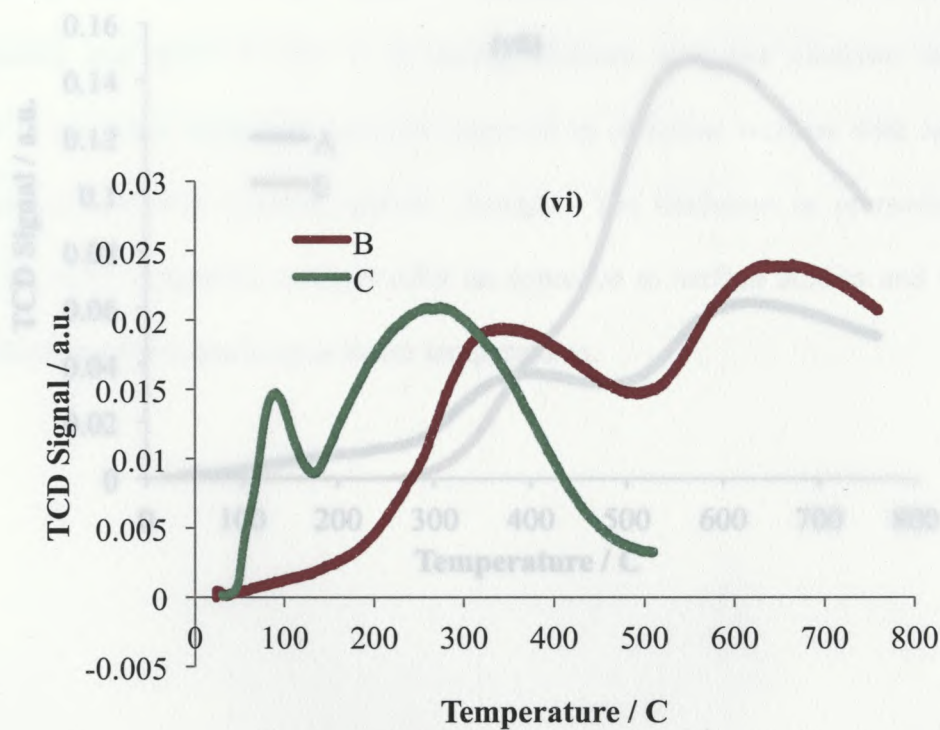
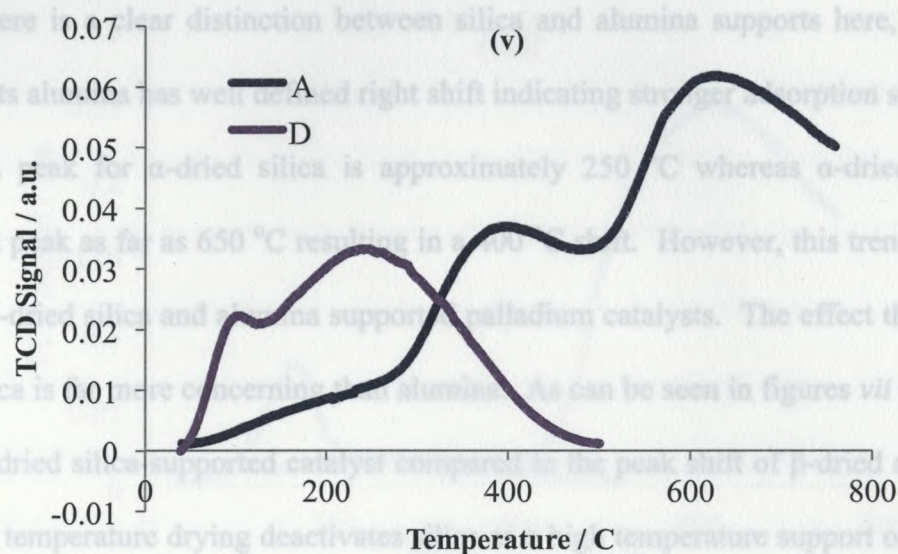




Multiple peaks observed from hydrogen TPD disclose availability based on bonding strength. The catalysts for figure *i* are  $\alpha$ -dried alumina supported palladium catalysts with desorption peaks at approximately 400 °C and 650 °C. The stronger bonding site is revealed at 650 °C and based on the right shifted trend; wet impregnation appears to favor full metal surface protrusion. This conclusion is observant in figures *ii-iv* as well. It is interesting to note that for catalysts observed in *iii*, there appears to be two distinct desorption sites as well as a sharper peak for incipient wetness. This could be the result of low temperature drying of the  $\beta$ -method as opposed to the oven drying. A comparison between supports was observed for figures *v* and *vi*.

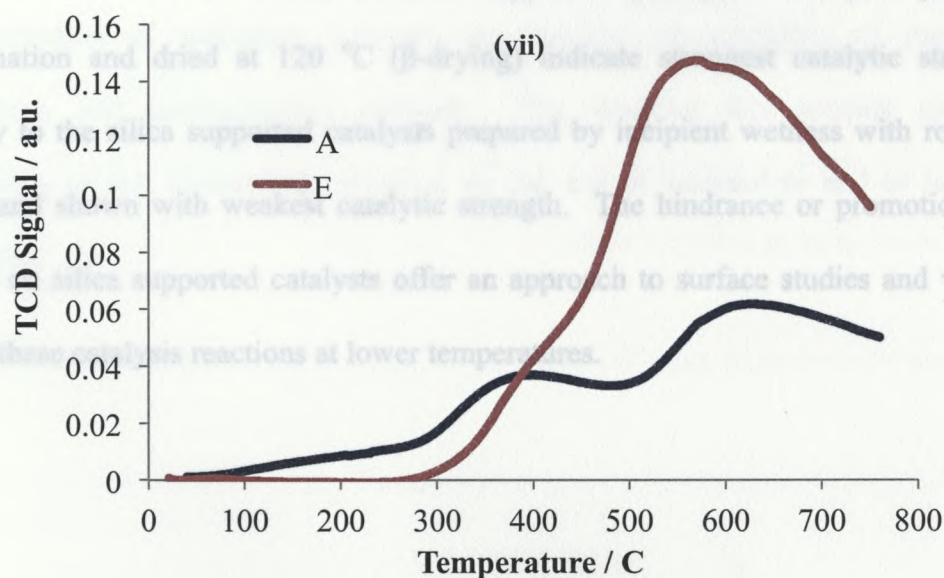




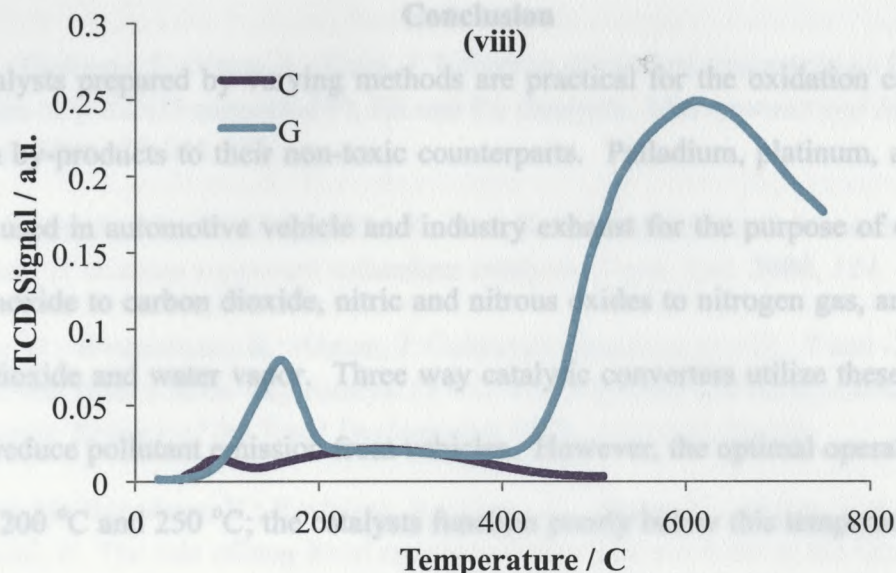




There is a clear distinction between silica and alumina supports here, and based upon TPD results alumina has well defined right shift indicating stronger adsorption sites. The highest desorption peak for  $\alpha$ -dried silica is approximately 250 °C whereas  $\alpha$ -dried alumina has a desorption peak as far as 650 °C resulting in a 400 °C shift. However, this trend is not observed between  $\beta$ -dried silica and alumina supported palladium catalysts. The effect the drying method has on silica is far more concerning than alumina. As can be seen in figures *vii* and *viii*, the peak shift of  $\beta$ -dried silica-supported catalyst compared to the peak shift of  $\beta$ -dried alumina indicates that lower temperature drying deactivates silica as a high temperature support or drying silica by oven promotes metal protrusion and exposure to the surface.







Based on TPD results, alumina supported palladium catalysts prepared by wet impregnation and dried at 120 °C ( $\beta$ -drying) indicate strongest catalytic strength which is contrary to the silica supported catalysts prepared by incipient wetness with room temperature drying and shown with weakest catalytic strength. The hindrance or promotion of the drying method on silica supported catalysts offer an approach to surface studies and variety that may benefit these catalysis reactions at lower temperatures.



## Conclusion

Catalysts prepared by varying methods are practical for the oxidation catalysis of toxic combustion by-products to their non-toxic counterparts. Palladium, platinum, and rhodium are commonly used in automotive vehicle and industry exhaust for the purpose of converting toxic carbon monoxide to carbon dioxide, nitric and nitrous oxides to nitrogen gas, and hydrocarbons to carbon dioxide and water vapor. Three way catalytic converters utilize these three metals to efficiently reduce pollutant emission from vehicles. However, the optimal operating temperature is between 200 °C and 250 °C; the catalysts function poorly below this temperature. It has been a growing interest to pursue a heterogeneous catalyst that functions well at the operating temperature of a standard vehicle as well as ambient temperature. Therefore, the preparation of low temperature oxidation catalysis was the primary goal for this study. Preparation and characterization of palladium catalysts are justified by alteration of support, promoter, atmosphere, and spectrographic methods. The resulting data provide insight on future engineering of low temperature catalysis for the use of automotive and or industrial exhaust production.

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